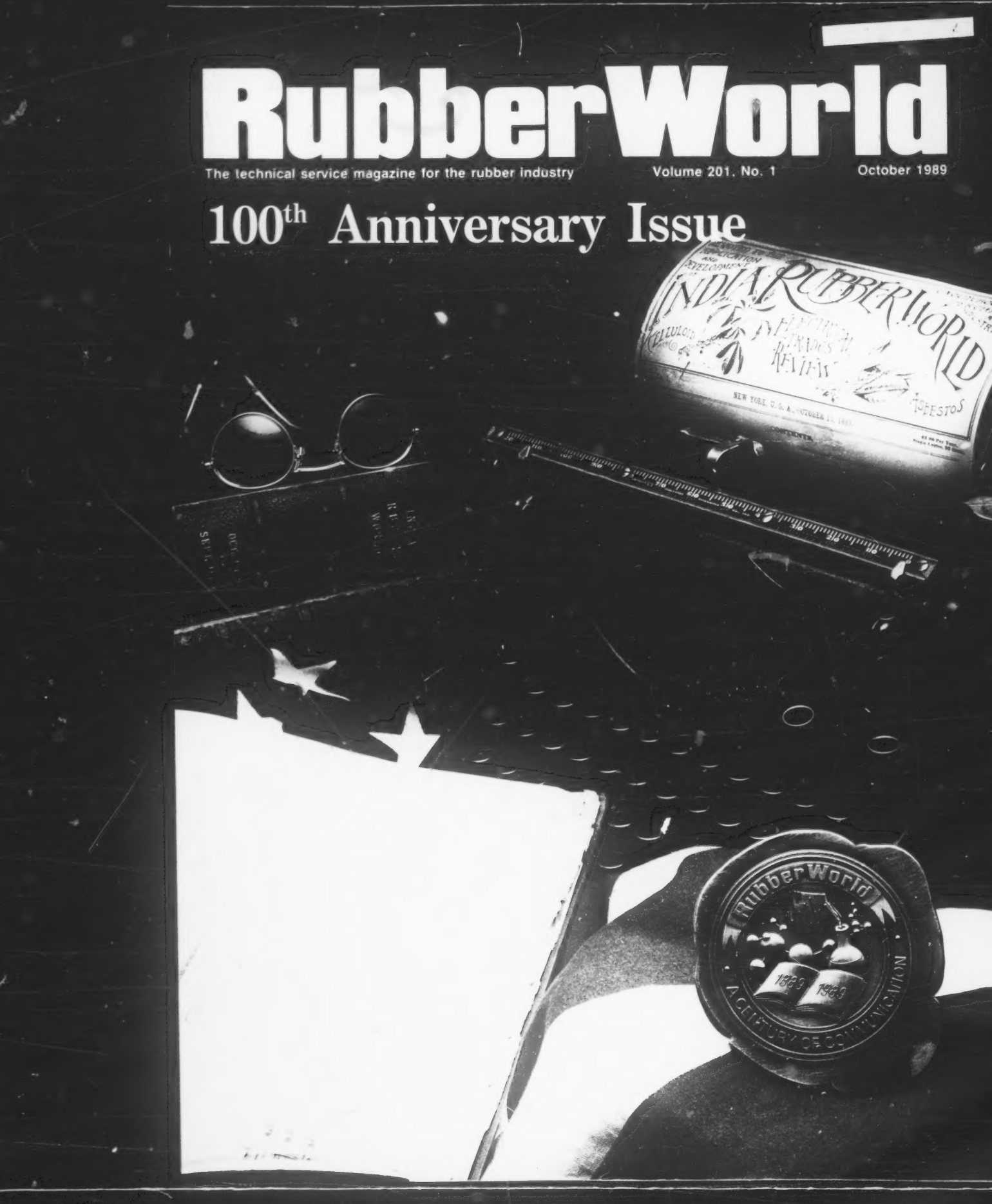
RubberWorld

The technical service magazine for the rubber industry

Volume 201, No. 1

October 1989

100th Anniversary Issue



100th Anniversary Issue

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The Audit Bureau

Editorial

Researching this issue was quite an eye-opener and on a few occasions a real eye-closer. When planning for this 100th anniversary issue, *Rubber World* had already printed 1,188 issues, of which almost all were perused by the editors. To read of the evolution of this industry on a month-to-month basis is remarkable, because it's not only an account of the progress of a material and an industry, but an account of extraordinary progress of the human species.

Going through those old issues was quite enlightening in other ways as well. In the October 1964 issue we read: "The place attained by these newcomers - the stereo diolefins, EPDM, epoxy rubbers, the urethanes and others still undiscovered - will be more clearly delineated in a subsequent article which will appear in October, 1989." An editor has a lot of nerve to say what's going to be covered 25 years into the future, but we were fearful that if we didn't cover these areas there would be some readers with great memories.

We feel we've covered all bases with contributions from Maurice Morton, John Sommer, Howard Stephens, H.L. Paris, Barbara Davies, Barbara Zimmerman and Dave Ewers, along with our own Walt Warner and Jon Menough. Speaking of covers, the cover of this issue has already won an award for Mayer Advertising. The cover was one of the first items planned for this issue and was actually created a year ago. The photo below shows some of the fine tuning on the cover shot being done by photographer Kim Henderson (left), Leonard Benner (center) the designer and myself.

Don R. Smith
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RubberWorld

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Business Briefs

The plant will have an initial annual capacity of 30,000 metric tons of tread and carcass grades of carbon black. P.T. Continental also has plans for expansion in the future.

Stamicarbon bv, the licensing subsidiary of **DSM**, and **Hyundai Petrochemical** of Seoul, South Korea signed a contract allowing Stambicarbon to supply technological know how for an LLDPE plant to be built in Korea. Stamicarbon will provide the process design, training and advisory services for the 60,000 t/y plant based on low-pressure solution technology (COMPACT process) expected to come on stream in 1991.

Rogers signed an exclusive licensing agreement with **Polimotor Research** for exclusive rights to the technology of the Polimotor engine for most major markets. Rogers has exclusive rights to produce and sell Polimotor engines in all commercial markets, including the automotive, marine and aircraft industries. Polimotor Research retains the rights to produce and sell Polimotor engines for competition racing and a developmental military diesel program.

Flexfab, Hastings, MI, and **Federal Hose Manufacturing**, Painesville, OH, formed a joint venture agreement to market silicone heater and coolant hose in addition to other silicone and flexible metal hose, ducts and connectors for the trucking and heavy duty equipment markets.

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Newbury Industries appointed **W.A. Bell & Assoc.**, Markham, Ontario, to represent its line of vertical- and horizontal-clamp injection molding machines in all eleven Canadian provinces.

J.M. Huber's Carbon Black Division appointed **Shelan Chemical** as its agent for furnace and thermal blacks in the northeast United States and Canada.

Dexter Adhesives & Structural Materials Division named **Rudolph Bros.** as distributor of Hysol aerospace paste adhesives in W. Virginia, Illinois, Ohio, Indiana, Michigan, Wisconsin, Minnesota and Kentucky.

Neville Chemical appointed **Durr Marketing Associates** as a manufacturer's representative for northwestern Pennsylvania, western New York, and West Virginia.

The Weighing Systems Division of **Sartorius Corp.** appointed **ASC/Aldinger** as an authorized scale dealer for Dallas, TX, and surrounding areas.

Corporate, financial news

Akzo increased prices of Perkacit TMTD from 8 percent to 11 percent; Perkacit TMTM from six to nine percent; Perkacit TETD from six to nine percent and Perkacit DPTT from three to six percent, effective Oct. 1.

Automotive Industries reported third quarter revenues of $12.5 million and a net loss of $3.6 million.

Bekaert Group achieved a consolidated net profit of

RMA tire report - June
(figures in thousands of units)

Passenger tires	YTD '89	YTD '88	% change
Shipments			
original equipment	28,511	28,272	0.8
radial	24,893	24,092	3.3
replacement	74,608	73,925	0.9
radial	70,711	68,905	2.6
export	6,471	4,840	33.7
radial	6,002	4,234	41.8
total	109,589	107,037	2.4
radial	101,605	97,231	4.5
Production	93,070	89,090	4.5
radial	86,646	80,598	7.5
Truck & bus tires			
Shipments			
original equipment	4,598	4,599	-
radial	3,809	3,379	12.7
replacement	17,178	16,228	5.9
radial	9,945	9,382	6.0
export	1,834	1,708	7.3
radial	1,373	1,337	2.7
total	23,610	22,536	4.8
radial	15,126	14,097	7.3
Production	20,273	18,572	9.2
radial	13,347	11,276	18.4

Natural rubber: Still going strong

by Barbara Davies, Malaysian Rubber Producers' Research Association

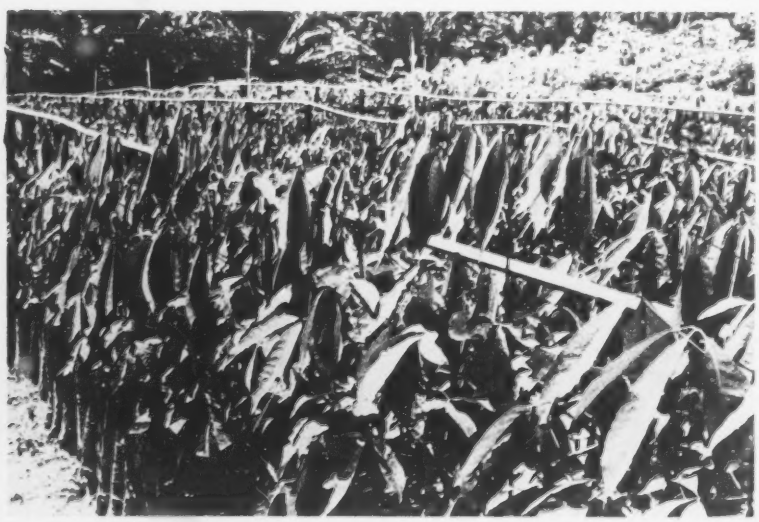
Natural rubber is the only rubber which can boast a history longer than that of *Rubber World*. 'Discovered' by Christopher Columbus in the fifteenth century, it remained a curiosity until 150 years ago when the twin discoveries of mastication and vulcanization established the basis of modern rubber technology. With the growth of rubber cultivation in South East Asia at the turn of the century, associated with the growing demand for tires for the first motor cars, natural rubber became a viable and profitable crop.

For its first five decades, the pages of *Rubber World* would have been filled with developments relating almost exclusively to natural rubber. The second five decades have seen enormous changes, with the advent of commercial synthetic rubbers which now hold 66% of the world market. The turning point came about 40 years ago, when, for various reasons, the share of synthetic rubbers started to climb and the growth of natural rubber production slowed down. In 1962 production of synthetics by the free world overtook that of natural rubber.

That natural rubber is still a vital raw material owes much to considerable advances in the science and technology of both production and end-use over the last 50 years, and to its inherent characteristics which still make it the material of choice in many applications.

Developments in production

The steady growth of natural rubber production from around 1 million tons in the late 1930s to over 5 million tons last year is due not only to the increased hectarage under rubber, but also to agricultural research. The original plantings of Hevea brasiliensis yielded about 250 kg/ha/yr - tree breeding and selection have raised potential yields to well over 3,000 kg/ha/yr. One of the most promising new clones being developed in Malaysia has yielded more than 5,000 kg/ha/yr in the preliminary evaluation stages. The newer clones not only give higher yields but are precocious yielders.



Grafting techniques are used for fast, cost-effective propagation of good planting materials. Such techniques are used successfully in commercial estates and have been introduced in the smallholder sector.

Average yields in the major natural rubber producing countries reflect the different structure of their industries. In the three major producing countries, smallholders predominate, but to different extents. In Malaysia they account for 75% of the industry, in Indonesia 85% and in Thailand 95%. Smallholdings tend to suffer from uneconomic size, low productivity and low capital.

Increased output in Indonesia and Thailand has come mostly from increases in hectarage: in the order of half a million hectares in each country since 1960. Yields have increased from 440 kg/ha/yr in 1970 to 480 kg/ha/yr in 1986 in Indonesia; the equivalent figures in Thailand are 300 kg/ha/yr and 630 kg/ha/yr. In Malaysia, on the other hand, there has been a drop in hectarage, but the average yield has increased from 800 kg/ha/yr in 1970 to over 1,100 kg/ha/yr in 1986, leading to a slight increase in overall production. This difference in productivity between Malaysia and the two other major producers is partly due to the fact that Malaysia was the first to undertake major replanting programs in the 1960s and early 1970s.

Two further important differences exist between Malaysia and the other major producers. Malaysia is the only one of these countries with an integrated system of research, development and advisory services covering both production and consumption aspects of natural rubber. The Malaysian Rubber Research and Development Board (MRRDB) is the parent body which directs and coordinates these activities, including the production research carried out by the Rubber Research Institute of Malaysia in Kuala Lumpur, the consumption orientated work of the Malaysian Rubber Producers' Research Association in the UK, and the Technical Advisory Service to consumers worldwide provided by the Malaysian Rubber Bureau. The second

difference, affecting smallholder productivity, is that in Malaysia over 400,000 hectares of smallholders land is within various organized land schemes. This enables smallholders to adopt modern agro-management practices and benefit from research, good infrastructure and social amenities. Yields in such organized schemes approach those of the estates, in Malaysia around 1,500 kg/ha/yr.

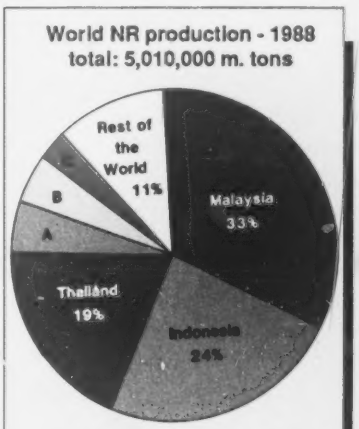
Recently efforts have been made to widen the genetic base of Hevea. The entire production industry is based on 22 seedlings derived from the material collected by Wickham over 100 years ago. An expedition in 1981 to Brazil organized by the International Rubber Research and Development Board has yielded about 14,500 seedlings, which may result in trees with superior characteristics and dramatic yield increases.

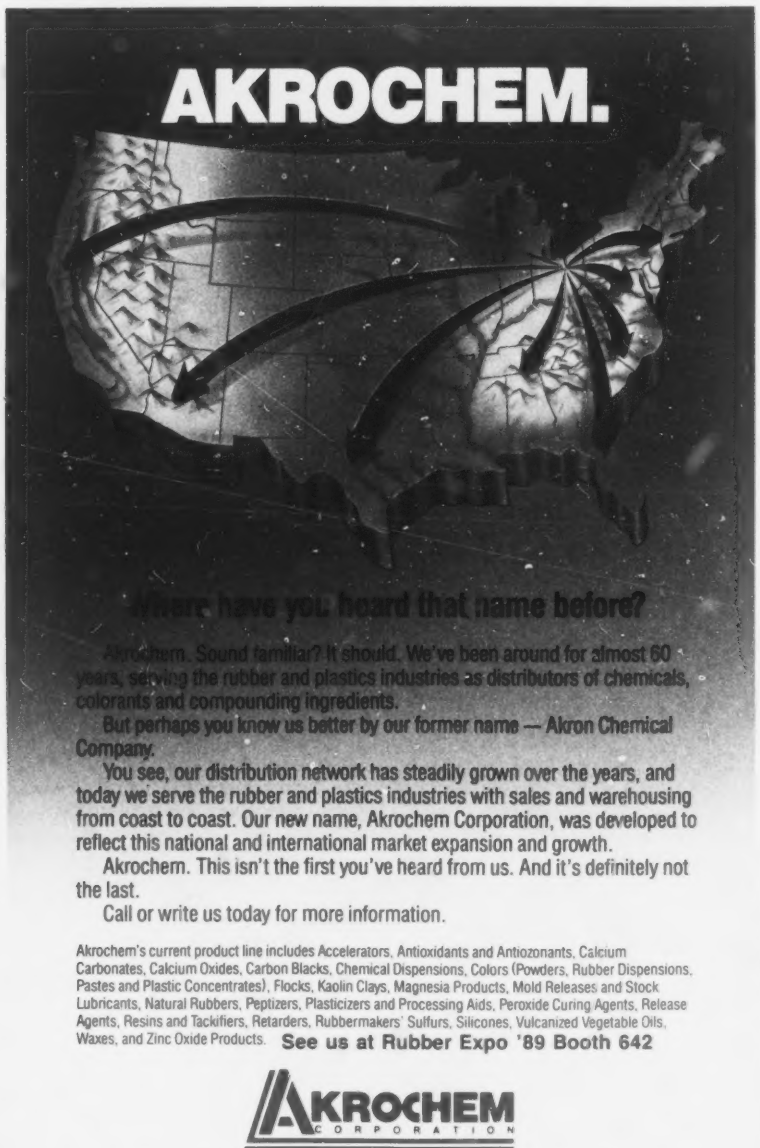
One of the most important advances in propagation techniques has involved the use of grafting to combine the best characteristics of two or more planting materials. This has resulted in the three-part tree: a high yielding trunk is grafted onto a vigorous root stock, and a disease resistant crown onto the trunk. This is now an established commercial practice which allows fast adoption of breeding innovations. A more recent advance is the use of tissue culture techniques: Hevea seedlings have been produced from somatic cells. Ultimately this could eliminate requirements for large nurseries, selection of seedling stocks and budding processes.

Productivity has also been increased by reducing the non-productive immaturity period of trees and by using chemical yield stimulants. Advanced planting materials, produced by budding and the use of core stumps, grow vigorously and uniformly when planted out and can be tapped after four years.

These young trees give high sustained yields with the use of adequate fertilizers and chemical stimulation. Ethylene-based stimulants were discovered in 1970, and their use increases yields throughout the life of the tree, even extending productive life of old trees in combination with controlled upward tapping.

Production can be constrained by labor shortages. Tapping needs skilled labor and less labor-intensive tapping systems have been developed. Half-spiral tapping every four to six days with stimulation gives yields at least as high as the current practice of tap-


World NR production - 1988
total: 5,010,000 m. tons
Rest of the World 11%
Malaysia 33%
B
A
Thailand 19%
Indonesia 24%
A - India 5% B - China 5% C - Sri Lanka 3%. (Percentages rounded to nearest whole number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ping on alternate days, with a labor saving of up to 70%; an added advantage is low bark consumption leading to longer tree life. Mechanization of tapping and collection systems is also being developed, with techniques such as motorized tapping and polybag collection.

Future concerns may include the development of clones suited to different climatic conditions. Work in China has shown that rubber can be grown as far north as 24°, beyond the established growing belt which extends just 15° either side of the equator. China is now the fifth largest producer, with over half a million tons per year despite relatively cool conditions and occasional typhoon winds and droughts. Recently, the RRIM has developed a computer system, Environmax, which recommends the best clones for different soil types and climatic conditions. However, possible changes in the global climate - the 'greenhouse effect' - are a relatively new concern: there are many uncertainties and major climatic changes would lie outside the scope of the current database. What is certain is that natural rubber production is environmentally sound, using renewable, non-polluting natural resources. Any increase in the hectarage of rubber worldwide may help to alleviate problems caused by large-scale destruction of the tropical rain forests.

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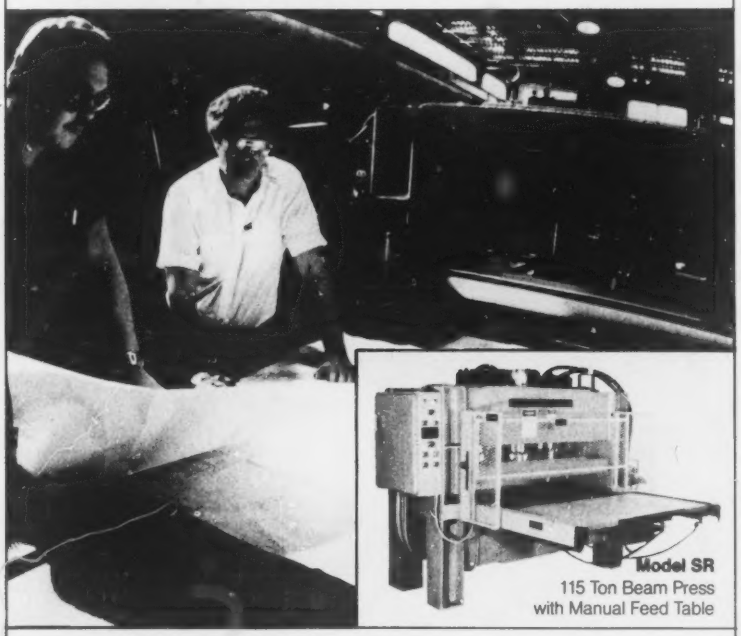

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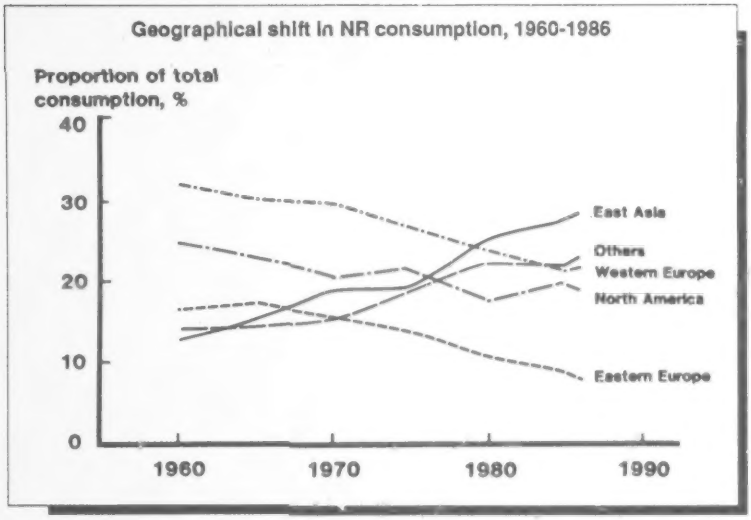
Market patterns

It is generally true that since the early 1950s all natural rubber produced has been sold. It therefore makes good economic sense to increase production in an orderly fashion, both to meet normal growth related to industrial expansion and to increase the market share of natural rubber vis-a-vis the synthetics. Here the activities of the International Natural Rubber Organization have been an important factor: two agreements in the last decade have ensured a degree of price stability and good returns for rubber growers, producing countries are thus confident enough to plan for increased rubber production and consumers are protected from wild price fluctuations.

It has been argued that on its techno-economic merits, natural rubber has the potential to take 42% of the market. Since 1950 natural rubber has been unable to meet increasing world demand for rubber (post-war demand was growing at 6% p.a., while natural rubber production increased at only a little over 2% p.a.) and has lost its predominant market position to the synthetics. Recently, total demand has slowed, with a consequent decline in synthetic growth rates and natural rubber growth remaining steady at 3.7% p.a. Its share of the market over the period 1980 to 1988 has consequently improved from 30% to 34%.

The geographical distribution of natural rubber consumption is changing: in particular, the newly industrialized and developing countries have become more important in the last two decades. Of special interest are the East Asian countries, which have increased their market share by more than 10% since 1970, from about 255,000 tons to over 500,000 tons. The most significant drop in market share has occurred in Western Europe. Consumption has grown only slightly



since 1970 to almost one million tons in 1987, a decline in terms of market share from 30% to about 20%. As well as the obvious growth in Taiwan, South Korea, Hong Kong and Singapore, the natural rubber producing countries are rapidly expanding their domestic rubber consumption. Malaysia, for example, is actively encouraging the growth of resource-based industries, and government policy in this area was laid down in the Industrial Master Plan of 1986. Advantages include purchase of raw materials at source, increased export earnings and added employment.

New materials

It is not enough for the natural rubber producers simply to produce more rubber. Attention must be paid to the needs of the consumers, in terms of quality, processability and presentation of the raw rubber, and the properties required of the final product. In the 1960s, when synthetic rubbers appeared to threaten the viability of natural rubber, the first moves were made in this direction with the development and introduction of the Standard Malaysian Rubber (SMR) scheme in 1965. The other major rubber producing countries have followed suit with their own technically specified rubber schemes, and natural rubber has been transformed from an agricultural commodity to an industrial raw material.

The SMR scheme has not remained static, revisions have been, and will continue to be made in response to consumer requirements and advances in production and processing technologies. Constant viscosity grades were introduced in 1969, and further improvements were made in 1979 when

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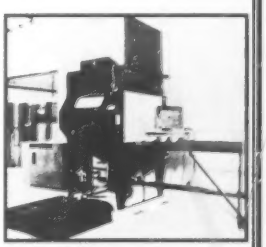

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the scheme was revised. This revision took account of demands for consistent processing within grades, by defining the raw materials going into each grade, introducing a cure indicator for all latex grades and tightening the rules for regrading. A new viscosity stabilized grade, SMR GP, was introduced, to provide a good quality easy-process rubber, potentially available in large volumes.

For the future, the technically specified rubbers will continue to evolve to meet the needs of the consumers. The current demand is for still greater processing consistency to maximize throughput in increasingly automated rubber product factories. At present SMR processing characteristics are indicated only by the PRI test and initial viscosity.

Current research at both RRIM and MRPRA aims to develop tests more directly indicative of processability which can be included as parameters in the scheme. Ultimately Malaysia intends to ensure that all its natural rubber, including latex, conforms to specifications relevant to consumer operations.

Developments such as technically specified rubber have ensured natural rubbers place in the field of general-purpose rubbers. Many attempts have been made over the years to chemically modify the natural rubber molecule and produce a new polymer with special properties. Some attempts have failed because processes have been uneconomical or a new synthetic material has been developed which, for one reason or another, has cornered the market. There have, however, been some success stories - rubber hydrochloride was manufactured commercially for over 30 years as a food packaging material; chlorinated rubber was used in paints; both depolymerized rubber and methacrylate graft copolymers are still in use today.

Until now, natural rubber has been unable to compete with the special-purpose rubbers in terms of properties such as oil resistance and low gas permeability. To meet these challenges, and that of the fastest growing sector, thermoplastic elastomers, new forms of natural rubber have been developed by MRRDB laboratories over the last decade. Both chemically modified epoxidized natural rubber and thermoplastic natural rubber blends are now commercially available.

With epoxidized natural rubber, the property/cost balance is right, and the competing synthetics have been in existence for some time, so the market area is well documented. In epoxidized natural rubber some of the unsaturation of the natural rubber molecule is converted to epoxide groups randomly distributed along the polymer chain. The process is applied in latex using low-cost ingredients, and is now being carried out commercially by Kumpulan Guthrie Sdn Bhd in Malaysia. Two grades, 25% and 50% epoxidized, are currently available under the trade name Epoxyprene.

Epoxidation raises the glass transition temperature of natural rubber and changes the polarity of the polymer. These factors lead to substantial property changes while maintaining the strain crystallizing nature, and therefore high strength of the base polymer.

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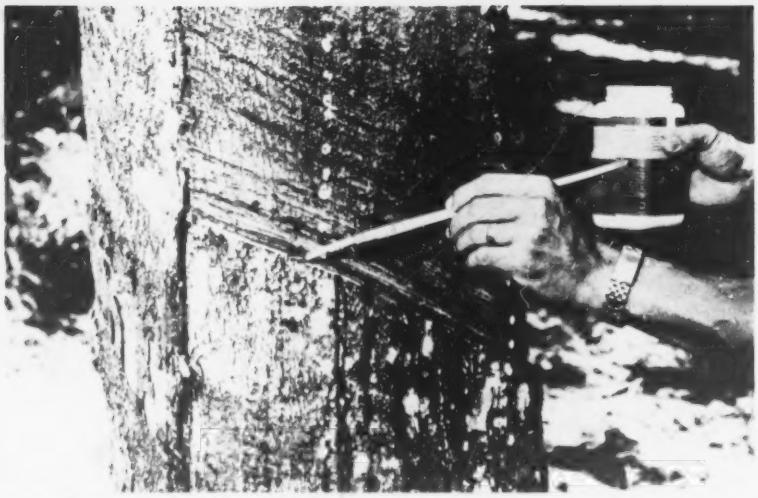

The use of yield stimulants painted on the tapping cut allows trees to be opened early for tapping and fine control of latex production.

The result is increased oil resistance, reduced gas permeability, high damping and compatibility with polar synthetic rubbers such as nitrile, polychloroprene and PVC, leading to good adhesion to these polymers.

Added advantages include good reinforcement by silica without the use of coupling agents, and an interesting combination of good wet grip and low rolling resistance. Its unique combination of properties suggest a wide range of potential applications for Epoxyprene, and some of these have already been extensively evaluated. Applications where light colors and high strength are required are of particular interest. Products investigated include milking inflations, conveyors, seals, tubing, vibration mountings, accoustic dampers, inner tubes, shoe soles and adhesives. The good wet grip and low rolling resistance have led to interest in the use of Epoxyprene for specialist pneumatic or solid tires.

Several attempts have been made to produce a viable thermoplastic natural rubber. Work at MRPRA over the last 20 years has resulted in some interesting materials, but these have either been insufficiently thermoplastic or not economically viable. The latest approach is based on the partial dynamic vulcanization of natural rubber blended with polyolefins, and has produced a material with good technical performance and attractive economics. These thermoplastic natural rubber blends are now being produced commercially, by Teknor Apex in the USA (Telcar DVNR) and Vitacom in the UK (Vitacom DVNR). They have attracted considerable interest in the important TPE market, currently growing at 8-10% per year.

The TPNR blends are characterized by excellent stress strain properties, high strength, good recovery and resistance to heat aging and ozone. Depending on the relative proportions of natural rubber and polypropylene, a range from soft thermoplastic elastomers to semi-rigid rubber-toughened plastics can be produced.

The cost/performance profile of the materials lies between the traditional olefinic materials and the 'engineering alloys'. Potential applications include replacement of rubber vulcanizates and other thermoplastic elastomers in products such as footwear and sports goods, and seals and hoses in the automotive sector. The latter is also the largest potential market for the hard grades, in applications such as bumpers, spoilers and body protection strips.

Other new materials from natural rubber are under investigation at MRPRA and elsewhere, of particular interest are further thermoplastic blends, an oil-resistant thermoplastic elastomer, and low molecular weight liquid rubbers, either as adhesives or as process aids for rubber.

End use research

Improving the consistency in processing of raw natural rubber and developing new materials from natural rubber are two important aspects of MRPRA's role in protecting and extending the market for Malaysian natural rubber. Other areas of work aim to improve formulations and processes, develop new uses, and generally protect the market from erosion by the synthetics. In the past, significant advances have been made in injection molding with natural rubber, the use of rubber in engineering applications, the development of oil-extended natural rubber (OENR) for winter tire treads and improved vulcanizing systems. All this has been backed by fundamental research which has helped the understanding of vulcanization, aging and properties such as elasticity, strength, abrasion and fatigue.

Past work on engineering applications has led to the acceptance of natural rubber as an engineering material, and the market is now one of the largest and fastest growing areas of non-tire natural rubber use. Current research on longevity and dynamic me-

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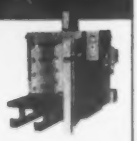

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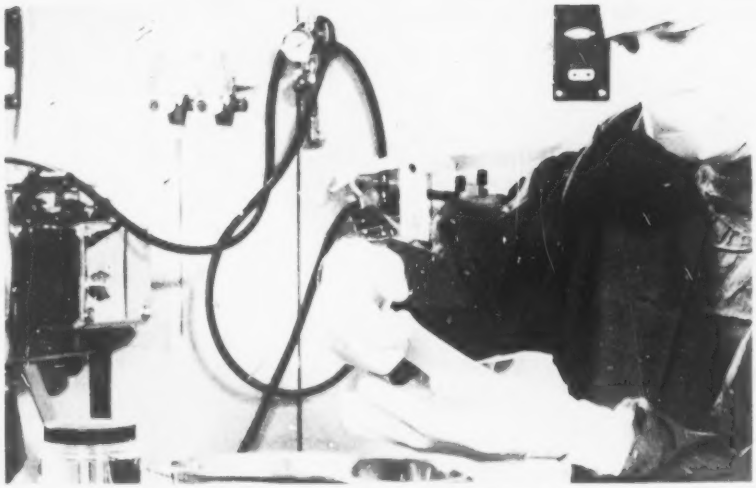
chanical properties has shown that natural rubber is superior to synthetic engineering polymers in many respects, and this basic work adds to the fund of knowledge used to promote natural rubber in engineering. Some interesting success stories include the world land speed record using natural rubber suspension, and the steel-laminated natural rubber bearings for the solid fuel booster rockets used in the space shuttle.

The most interesting development in civil engineering applications, and one with great market potential, is that of earthquake protection. The idea arose about 15 years ago, following widespread adoption of steel-laminated natural rubber bearings for bridges and buildings. Initial computer studies established that the thinking was sound, and MRPRA then instituted extensive development and testing work in collaboration with the Earthquake Engineering Research Center at the University of California, Berkeley. The resulting system was adopted for the Foothill Communities Law and Justice Center in San Bernardino.

This building has been subjected to minor earthquakes and has responded well compared to conventionally protected structures, greatly reducing the forces transmitted to the building. The system differs from other proposed base isolation systems in that the rubber is specially designed to eliminate the need for additional mechanical dampers or wind sway prevention devices.



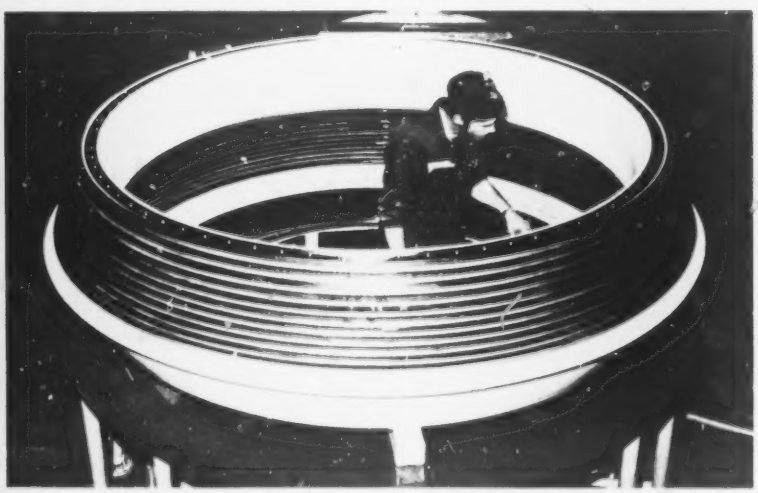
The recent surge in demand for examination and surgeons gloves created high demand for natural rubber latex.

The stability of natural rubber over a wide range of temperatures and frequencies is essential for successful implementation. The system is now being installed in the Los Angeles County Fire Department Control Center and is being considered for several other emergency service buildings in California. Interest is also high in Japan and Europe.

Work has been resumed on OENR in tire treads. Originally developed in the 1970s to provide enhanced grip in ice and snow, OENR is now being assessed in the light of more recent developments: all-season tires and the requirement for low rolling resistance. Compared with standard synthetic compounds, OENR offers improved wear performance at low temperatures, lower rolling resistance and equivalent wet traction, as well as improved snow and ice traction. A slight disadvantage in summer wear rates is more than offset by the low rolling resistance and the low wear in winter.

The wet grip and rolling resistance properties of epoxidized natural rubber have been mentioned already, and MRPRA is assessing its performance in tire treads. Wear performance has been improved by blending with butyl rubber, but at the expense of a slight loss in wet traction. Blends with other polymers and the use of black/silica combinations are now being considered.

A relatively new area of tire research is that of improving natural rubber formulations for truck tire retreads. At one time natural rubber was the preferred material, but its position in this important market has been gradually eroded because of the widespread use of precured retreading where synthetic rubbers are favored. In this process, the good building tack of natural rubber is not a primary consideration, and the profile of the tread reduces the need for natural rubber's low heat-build-up properties. The favored SBR/BR precured retreads give excellent wear performance in long-haul low-severity conditions. New reversion-resistant natural rubber based compounds have been shown, both in



Nozzle bearings for the solid fuel booster rockets of the space shuttle were manufactured from steel laminated NR.

the laboratory and in fleet trials, to outperform the best synthetic treads under a range of service conditions. A major UNIDO-funded project is now underway, involving the building and testing of precured truck tire retreads in the UK and five other countries. Technologists from the rubber producing countries are being trained using the latest retreading equipment, thus contributing to technology transfer.

The most important area of use for natural rubber after tires is in latex applications, and consumption is growing at about 5% per year. Malaysia supplies about 75% of the world's natural latex: about 20% of her natural rubber production is in the form of latex concentrate.

The RRIM and MRPRA are actively involved in improving the properties and quality of the raw material and its products, as well as advising manufacturers on latex use. Areas of research include viscosity and stability, prevulcanization, leaching and lubrication. The current surge of commercial interest in the manufacture of dipped disposable examination gloves has led to work aimed specifically at improvements in the production process for examination gloves. Also of topical interest is the bacteriocidal nature of natural latex foam: here it shows a distinct advantage over polyurethane foam: this could become a 'selling point' to recover some of the market lost to the synthetic material.

Health and safety legislation is now affecting all areas of manufacturing and rubber is no exception. Most of the current interest is in nitrosamines, particularly in baby soothers and teats, in gloves, food contact applications and toys. Raw natural rubber is free of nitrosamines and nitrosatables, and formulations can meet all the current North American and European regulations. Teats and soothers have also been tested for strength properties: natural latex teats have tear, tensile and puncture strengths two to three times greater than silicone teats. The former should therefore meet the requirements of a bite test being developed by the British Standards Institution.

Looking to the future, an area of major importance is likely to be that of polymer blends. Some have said that the development of new rubbers is unnecessary - an almost infinite range of vulcanizate properties may be obtained by blending existing polymers. To be successful, this approach must achieve the correct morphology and optimum crosslink distribution. MRPRA is already working in this area, with a new characterization technique to measure crosslink densities in the separate phases of blends. Once this can be accurately measured, it should be possible to adjust distribution by changing the rubbers and/or curing systems, and ultimately improve blend properties.

Prospects for NR are bright. Research and development has enabled the producing industry to meet demand in terms of both quantity and quality, and enabled consumers to make the best use of top quality materials.

There is no doubt that, with the backing of science and technology, natural rubber will continue to meet the challenges of the competitive world of modern polymers.

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SR - past, present and future

by Maurice Morton, Regents Professor Emeritus of Polymer Chemistry, The University of Akron

Unlike the other synthetic polymers, synthetic rubber was developed to duplicate an already known material, i.e., natural rubber. The latter was actually discovered in America as a result of Columbus' voyages, but did not enter into industrial technology until the early part of the 19th century, i.e., after the development of vulcanization. Since then there were continuous attempts to synthesize this unique elastic material by chemical methods. Incidentally, the name "rubber" is also unique to the English language, most other languages using some form of the original name ("caa-ochoe") used by the American Indians, and is said to have originated in 1770 with Joseph Priestley, who found this material useful in erasing pencil marks.

Early history

Long before the rise of synthetic polymers, which followed Staudinger's discovery of macromolecules in the 1920s, there were many attempts to synthesize rubber. These started shortly after Williams' classical analysis (ref. 1) of natural rubber in 1860, which showed it to consist of isoprene and its homologs. Both Bouchardat (ref. 2) and Tilden (ref. 3) then tried to "convert" isoprene into a rubberlike substance, using heat and strong acids, with little success.

Other investigators then tried using other dienes, e.g. butadiene, 2,3-dimethylbutadiene and piperylene, but were no more successful.

The first synthetic rubber to merit industrial production was the famous (or rather infamous!) "methyl rubber" produced in limited tonnage in Germany during the emergency of World War I. This was a polymer of 2,3-dimethylbutadiene produced by thermal polymerization at 30-70°C in a process lasting from 2-6 months! This rubber was so bad that it was dropped immediately after the war.

First real synthetic rubber

During the 1920s, Staudinger's classic work on polymers and polymerization led to a more intelligent approach to the problem of synthetic rubber.

Thus, both in Germany and the USSR, the polymerization of butadiene by sodium metal produced the first commercial synthetic rubber, called "Buna" rubber, for obvious reasons. The Russians stayed with sodium polybutadiene for the next two decades, until the end of World War II, while the Germans changed over to the emulsion copolymerization of butadiene and styrene during the 1930s. This was still called "Buna" rubber, although they indicated the comonomer styrene by the name "Buna S". (They also developed nitrile rubber at that time, by the copolymerization of butadiene and acrylonitrile, naming it "Buna N".)

It was Buna S that was the basis for the rise of the giant synthetic rubber industry in the United States during the rubber emergency of World War II, starting with the shutdown of the supply of natural rubber from the Far East after Pearl Harbor.

Prior to that, there was no real interest in general-purpose synthetic rubber in the U. S., the only developments being in special oil-resistant rubbers, such as Thiokol in 1930 and Neoprene in 1932.

The phenomenal rise in production of butadiene-styrene copolymer in the USA between 1942 and 1945 represented a remarkable feat of technology, second only to the development of the atomic bomb, and led to a complete change in the world picture.

At that time, the U. S. was consuming about 1 million tons of natural rubber per annum, or roughly one-half of the world supply. We had a stockpile of about a one year's supply. The Government Synthetic Rubber Program then spent $700 million to build 51 plants to produce the necessary synthetic rubber to meet that demand, starting virtually from scratch. How successful that effort was is shown in table 1 (refs. 4 and 5). Today, this useful tire rubber is the dominant synthetic rubber and is the main component of automobile tires.

At the same time as the above developments in the rise of butadiene-styrene rubber, the Standard Oil Company (ref. 6) also used its contacts with the German company, IG Farbenindustrie, to obtain information leading to the development of butyl rubber. This was the first of the low-unsaturation synthetics so necessary for rubber of superior weathering properties.

Table 1 - world SR production 1933-45 (thousands of long tons)

Year	USSR (SK rubber)[a]	Germany (Buna S)	USA (GR-S)[b]	Canada (GR-S)
1933	2.2	----	----	----
1934	11.1	----	----	----
1935	25.6	----	----	----
1936	44.2	----	----	----
1937	25.0	2.1	----	----
1938	53.0	4.0	----	----
1939	78.5	20.6	----	----
1940	----	37.1	----	----
1941	----	65.9	0.23	----
1942	----	94.2	3.7	----
1943	----	110.6	182.3	2.5
1944	----	97.5	670.3	32.1
1945	c	----	719.4	36.6

[a] Sodium polybutadiene

[b] Wartime name for butadiene-styrene copolymer (now SBR)

[c] At the conclusion of the war, the USSR was producing about 100,000 tons of SK rubber.

Recent developments

The last 25 years witnessed two giant advances in synthetic rubber and rubber technology:

- stereospecific polymerization, and
- block copolymers (thermoplastic elastomers).

Stereospecific polymerization, i.e. the synthesis of such "stereo" rubbers as cis-1,4-polyisoprene (natural rubber) and cis-1,4-polybutadiene, as well as of the ethylene-propylene copolymers (EPDM), was the result of a revolutionary discovery of stereospecific polymerization catalysts by Ziegler in Germany and Natta in Italy. Block copolymers, especially the styrene-butadiene-styrene triblock copolymers which lead to thermoplastic elastomers, arose from the application of "living" anionic polymerization systems. This development opened a whole new area of rubber products, where the rubber is permanently thermoplastic, because it consists of a two-phase material in which a plastic component (e.g., polystyrene) is finely dispersed within the rubber matrix, to which it is chemically bonded, and thus acts as a thermoplastic crosslinking agent. This, then, made injection molding a viable technology in the rubber industry.

Synthetic rubber today

The role of synthetic rubber today is well illustrated by looking at rubber consumption in the USA. We produce a total of about 2 million metric tons of synthetic rubber per annum (of which about 2/3 consists of the two principal tire rubbers, SBR and polybutadiene). In contrast, the U.S. consumption of natural rubber represents only about 1/4 of total rubber use. On a world scale, the ratio of natural to synthetic is somewhat more favorable (about 1/3).

Synthetic rubbers today fall into two broad categories, which govern their technology. These are:

- Rubber vulcanizates, where the original long-chain macromolecules are crosslinked into a permanent net-

Table 2 - synthetic rubber vulcanizates

Name	Chemical name	Chain unit structure	Vulcanizing agent	Properties and uses
SBR	Butadiene-styrene copolymer	$[(CH_2\text{-}CH{=}CH\text{-}CH_2)_3CH_2\text{-}CH(C_6H_5)]$	Sulfur (peroxides)	General purpose, mainly for tires.
Polybutadiene	Polybutadiene	$[CH_2\text{-}CH{=}CH\text{-}CH_2]$	"	Excellent tire tread wear, low temp. prop.
Polyisoprene	Polyisoprene	$[CH_2\text{-}C(CH_3){=}CH\text{-}CH_2]$	"	General purpose, same as natural rubber.
EPDM	Ethylene-propylene-diene copolymer	$[(CH_2\text{-}CH_2)(CH_2\text{-}CH(CH_3))_1\text{-diene-}]$	"	Excellent weathering. Wire and cable, one-ply roofing.
Nitrile	Butadiene-acrylonitrile copolymer	$[(CH_2\text{-}CH{=}CH\text{-}CH_2)_{2\text{-}8}(CH_2\text{-}CH(CH{\equiv}N))]$	Sulfur	Oil resistance. Gasoline hose, automotive engine parts.
Butyl[a]	Isobutene-isoprene copolymer	$[(CH_2\text{-}C(CH_3)_2)_{50}CH_2\text{-}C(CH_3){=}CH\text{-}CH_2]$	Sulfur	Low air permeability good aging. Tires, insulation.
Neoprene[b]	Polychloroprene	$[CH_2\text{-}C(Cl){=}CH\text{-}CH_2]$	Metal oxides or diamines	Oil resistance, high gum strength. Molded parts, rubber hose and gloves.
Polyurethanes	Polyurethanes	$[OROC\text{-}NH\text{-}R'\text{-}NH\text{-}C(=O)]$	Urethane functional groups	Excellent abrasion resistance, range of hardness. Footwear, toys, foam.
Fluorocarbon	Fluorocarbon copolymer	$[(CH_2\text{-}CF_2)(CF_2\text{-}CF(CF_3))]$	Diamines	Excellent heat and solvent resistance. Used for extreme conditions.
Silicone	Polysiloxanes	$[Si(CH_3)_2\text{-}O]$	Peroxides	Retention of prop. over broad temp. range. Gaskets, tubing.

[a] Includes chlorobutyl and bromobutyl
[b] Includes Hypalon (a chlorosulfonated polyethylene)

work by reaction with a chemical crosslinking agent (vulcanization). These are the descendants of Charles Goodyear's original process of sulfur vulcanization of natural rubber.

• Thermoplastic elastomers, where the rubber chains are bound into a network held together by thermoplastic domains, and which can therefore be molded and remolded by heat.

The rubber vulcanizates

The most recent edition of Rubber Technology (ref. 7) provides a good idea of the large variety of synthetic rubbers available today. These are listed, by type, together with their chemical structure and properties in table 2. No attempt was made to show the various grades available for each elastomer, since these generally comprise large numbers, and are available in the industrial literature.

An examination of table 2 reveals two remarkable features: a) the wide range in properties (and uses) of the various synthetic rubbers, and b) the variety of crosslinking agents required to vulcanize the elastomers.

It is obvious that synthetic rubbers today offer a wide variety of physical and chemical properties not obtainable from natural rubber. Thus the legendary impermeability of butyl rubber to air has revolutionized tire construction. The impressive oil and solvent resistance of nitrile has enabled the use of rubber in many necessary applications, including the ubiquitous gasoline hose at service stations. The silicones, with their unique molecular structure of alternating silicon and oxygen atoms, have enabled the use of rubber over a broad range of temperatures, from sub-zero (refrigerator door gaskets) to oven heat (200°C). Then we have the unbelievable fluorocarbon rubbers, with their ability to resist a variety of solvents as well as temperatures as high as 300°C (48 hrs.) and 200°C for continuous use.

The unique "castable" polyurethanes exhibit amazingly high resistance to abrasion, a highly desirable property for footwear and toys, subjected as these products are to the known destructive propensities of feet and kids, respectively. The highly saturated hydrocarbon rubbers, butyl and EPDM, have brought a new dimension into the long-term aging and weathering of rubber insulation. In fact, EPDM rubber is enjoying a rapid growth as single-ply roll-roofing material, replacing the venerable asphalt-impregnated roofing.

Some of the more recent developments in synthetic rubber have been equally exciting. Thus the hydrogenated nitriles have added the extra aging property of saturated hydrocarbons to the well-known solvent resistance of the nitriles. The propylene oxide rubbers have unusually high resistance over a range of temperatures, even better than natural rubber, as well as good ozone resistance. The polyalkylene sulfides, one of the first synthetic rubbers produced in this country, have outstanding solvent, aging and ozone resistance.

As for the vulcanization process, it is obvious from the list in table 2 that the crosslinking of synthetic rubber chains into networks has gone far beyond the original sulfur-based process

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pioneered by Charles Goodyear in 1839. This is natural rubber, and can be crosslinked by other agents. Thus the chlorine-containing Neoprene is best crosslinked by the reaction of the allylic chlorine atoms (from 1, 2-enchainment) with metal oxides, such as magnesium or zinc oxide. Diamines can also react with this polymer, as a crosslinker, and the same reaction can be carried out with the chlorine or bromine atoms of the halobutyls. As a matter of fact, one of the methods for making otherwise incompatible blends of butyl with natural rubber or SBR is to use chlorobutyl or bromobutyl in a zinc oxide/sulfur vulcanization system. Diamines are also the crosslinkers for the fluorocarbon rubbers, by reaction with the active fluorine atoms on the polymer chains.

When the polymer chain has no satisfactory reactive points, such as active side-groups or double bonds, the organic peroxides can be relied on to crosslink the chains. Hence peroxide vulcanization is used for silicone rubber and for some of the low-unsaturation hydrocarbon rubbers. This type of crosslinking depends on the ability of the peroxide to abstract hydrogen atoms from hydrocarbons, creating radicals along the polymer chain, and these subsequently couple to form crosslinks. Hence this method is useful when no other reactive groups are available as substituents on the rubber molecule.

The thermoplastic elastomers

This class of synthetic rubbers had its start approximately 25 years ago as a development of anionic "living" polymerization (refs. 8 and 9). The latter refers to the polymerization of monomers, such as butadiene, isoprene, styrene, etc., by organometallic initiators, preferably of the lithium type. These systems are referred to as "living" since each initiator molecule is capable of starting a polymer chain, which then continues to grow as long as any monomer is available. In other words, with suitable precautions, the growing chains never terminate (or "die"). Hence, these are ideal systems for the synthesis of block copolymers, by sequential addition of different monomers.

The type of block copolymers which originally gave rise to the thermoplastic elastomers were the triblock copolymers, polystyrene-polybutadiene-polystyrene (ref. 10), developed by the Shell Chemical Co. under the tradename of "Kraton." A schematic of the molecular structure and morphology of these materials is shown in figure 1. As can be seen, the polystyrene blocks, being incompatible with

Figure 1

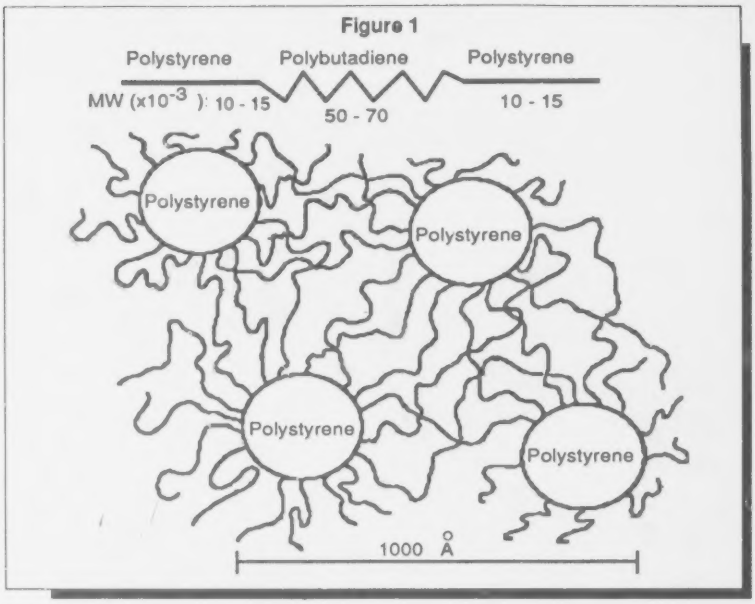

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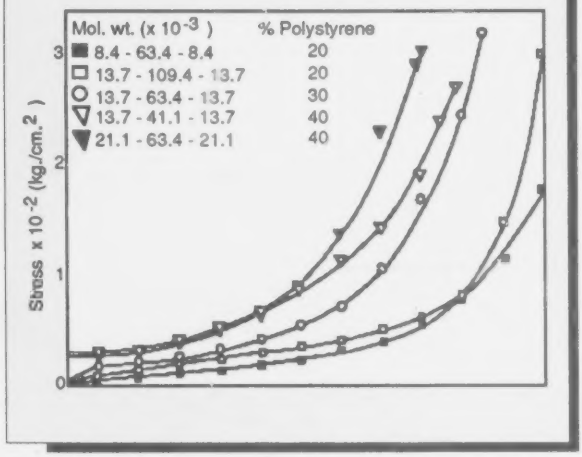
Figure 2



the polybutadiene, separate out as domains dispersed in and chemically bound to the polybutadiene matrix, thus forming a rubber network held together by thermoplastic polystyrene "crosslinks." It is not surprising, therefore, that such a material exhibits the properties of a vulcanized rubber at moderate temperatures (resistance to flow, good retraction, etc.) but flows freely at elevated temperatures.

The tensile properties of such thermoplastic rubbers are well illustrated in figure 2 and table 3 for a series of styrene-isoprene-styrene triblock copolymers of varying composition and molecular weight (refs. 8 and 9). It can be seen that the modulus of these rubbers is governed mainly by the polystyrene ("filler") content, more or less independently of molecular weight, while the tensile strength is largely independent of both factors, except at very low molecular weight of the polystyrene. What is also notable is the very high strengths obtainable in these materials. This is undoubtedly due to the high regularity of block size obtained in anionic polymerization, leading to a very uniform morphology, which, in turn, results in a uniform network structure. The sharp drop in tensile strength at low polystyrene levels is obviously due to the much greater compatibility of the short polystyrene chains with the polyisoprene, resulting in a homogeneous rather than a two-phase morphology, to the point where a network no longer exists.

The development of these triblock copolymers thus gave rise to a whole new concept of "thermoplastic rubber," where a network of "soft," rubbery chains is held together by a dispersion of a "hard" thermoplastic phase. Since then, this concept has been applied to a variety of block and graft copolymers having different properties tailored to specific uses. For example, although the styrene-diene triblock copolymers can be ideally

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synthesized by anionic polymerization, they suffer from the poor temperature and solvent resistance of the polystyrene and the poor aging of the polydiene. (This has been somewhat improved by hydrogenation of the polydiene blocks.) Unfortunately, the anionic mechanism of polymerization is limited to very few practical monomers. Hence other approaches have been used.

One highly desirable thermoplastic elastomer (TPE) is, of course, a block (or graft) copolymer of EPDM and polypropylene, which would have the good aging of the EPDM and the good temperature and solvent resistance of the polypropylene "crosslinks." However, it has not been found possible to create such a block copolymer by a "living" polymerization method. Instead, a mixed block and graft system can be made by subjecting a mixture of the two polymers to high shear at elevated temperature, at which point the linear polymer chains are continuously ruptured and recombine into various block and graft copolymers. The morphology of such materials is much more irregular than that of the anionic triblocks so that tensile strength drops, as expected, but the desirable improvement in resistance to temperature and solvents of the "olefinic TPE's" is notable.

Table 3 - tensile strength of SIS block copolymers

Wt. % styrene	Molecular wt. ($\times 10^{-3}$) S	I	S	Tensile strength MPa
40	21.1	63.4	21.1	31.0
40	13.7	41.1	13.7	30.6
30	13.7	63.4	13.7	32.1
20	13.7	109.4	13.7	27.0
20	8.4	63.4	8.4	16.0
19	7.0	60.0	7.0	2.2
11	5.0	80.0	5.0	0

Using various polymerization and interpolymer reactions, a constantly increasing array of thermoplastic elastomers has become available during the past decade or so. A list of commercially available types is shown in table 4, but this may already be outdated by the time of publication of this article, since this is a rapidly expanding field! As can be seen, these TPEs have been classified according to the nature of the "soft" and "hard" segments making up their structure, since their thermal and solvent resistance are mostly dependent on the nature of the "hard" blocks, which form the network junctions, and these can be either crystalline or amorphous. No attempt has been made to list all of the products by trade names, but the latter may be found in the appropriate technical publication (refs. 11 and 12).

The future

The art of forecasting may appear to be quite difficult but is actually relatively simple. Since "the future" usually encompasses a period of anywhere from 20 years to centuries, the time of reckoning is quite far away (and often past the lifetime of the prophet)! Hence, if the prophecy is proven completely wrong, no one would remember it anyway. But should it actually be vindicated, there could always be

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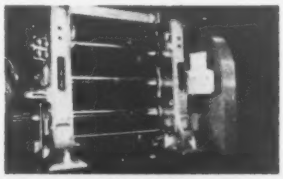
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Table 4 - classification of commercial thermoplastic elastomers

Nature of hard phase	*Type of polymer*	*Chemical composition*	
		Hard phase	*Soft phase*
Amorphous	Triblock (SBS)	Polystyrene (s)	Polybutadiene (B)
Amorphous	Triblock (SIS)	Polystyrene	Polyisoprene (I)
Amorphous	Triblock S-EB-S)*	Polystyrene	EB copolymer*
Crystalline	Multiblock	Polyester	Polyester**
Crystalline	Multiblock	Polyurethane	Polyether (or polyester)
	Multiblock		
Crystalline	Multiblock	Polyamide	Polyether
Crystalline	Graft/blend	Polypropylene (or polyethylene)	EPDM

*EB refers to poly(ethylene-co-butene-1)
**Amorphous polyester

some scholar who may discover it in the literature and loudly marvel at the remarkable powers of the long-gone soothsayer.

In the case of synthetic rubber, it might be best to consider possible future developments separately for the vulcanizates and for the thermoplastic elastomers.

The rubber vulcanizates

On reviewing the array of vulcanizates listed in table 2, one has the feeling that there is now available a variety of polymer chain structures offering a wide range of chemical and physical properties.

It is difficult to see what new types of chain structures could be developed that would offer substantial improvements in properties and still be economically feasible. Short-range improvements in base polymer, compounding and vulcanization can be expected in the immediate future, but revolutionary changes in the distant years are difficult to anticipate.

The most challenging problem in rubber technology is the creation of a rubber which could withstand ultra-high temperatures, i.e., ca. 1000°C. This has been a goal of aerospace scientists and engineers for many years, since such a material would be of special importance for use in rocket engines, etc.

It is obvious that organic polymers could not fill this need; the question is whether an "inorganic" polymer could be developed having the necessary rubbery properties. To date a number of inorganic materials have been used for such applications, but these have been rigid ceramics, not rubbers. Hence the solution of this problem lies in the future.

The thermoplastic elastomers

Since this development is so recent, it is not difficult to predict that it has a very promising future. This is especially true because of the unique potential of these materials.

In the first place, they have enabled the use of rapid molding methods, e.g., injection molding, for the manufacture of rubbery products. Secondly, they can be used to prepare a range of materials, from soft to hard rubbers all the way to high-impact plastics.

The combinations of the various polymers shown in table 4 represent only the beginning of a new technology. As a matter of fact, these materials are sometimes referred to as "elastoplastics" instead of thermoplastic rubbers.

The significance of this is that it is leading to the disappearance of the boundary between rubber and plastics, and this is of special relevance to the automotive industry, which is one of the major consumers of these materials.

Both in the short term and from a long-range view, therefore, these materials appear to represent the "wave of the future."

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Developments in compounding

by Howard L. Stephens, Emeritus Professor of Polymer Science, The University of Akron

The problem of estimating the future needs when related to compounding depends on the compounder's relationship to his working environment.

Perhaps this is best illustrated by the diagram described by B.S. Garvey, Jr. in the first edition (1959) of "Rubber Technology" (figure 1).

However, it is obvious from the flow diagram that only a large organization would have all of the departments as shown above. Smaller companies in many instances do not have research groups to back up product development and production.

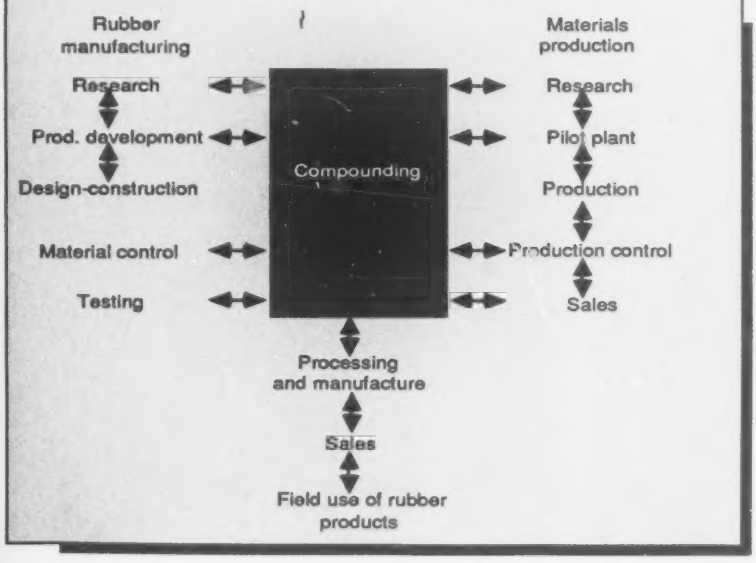
In these instances, the chief compounder (or only compounder) has to depend on the information received from material manufacturers and suppliers. But the diagram does reflect the ideal situation regarding compounding in the 1980s and in future years even though the idea was written over 30 years ago. The compounder's function is best described in the 1978 Vanderbilt Rubber Handbook as follows:

"He must be able to select the proper elastomers and additives available to meet the conditions of the finished product. This requires a thorough understanding of the following:

- Properties of the elastomers available.
- Vulcanization or curing systems to give the potential properties needed.
- Modifying materials which give the required physical properties and aging resistance.
- Compounds must be able to process properly depending on processing equipment.
- Commercial compound design, and
- How to test and evaluate raw materials and finished products."

From this standpoint, the compounder must be well aware of the changes being made in the production and availability of elastomers and the ingredients used in rubber manufacture. This will be the basis for the following discussion in this article.

Figure 1 - flow diagram circa 1959



Availability of ingredients

A survey was made using the "Blue Book: Materials, compounding ingredients, machinery and services for rubber" for three periods, 1968, 1980 and 1989 to illustrate the changes occurring in the industry over this period of time in order to show trends that occur due to OSHA requirements, buy-outs and mergers.

Naturally, this source has changed its contents over this time period, however, the trends are still a good indication of how the industry has changed or may change during the next decade or two. The number of suppliers has increased over the past 10 years, as indicated in table 1.

From this information, it is obvious that there is still a large increase in the number of suppliers over this period, and furthermore, the growth in the use of custom mixers has increased 230%, indicating that this is a cheaper way of processing or that the custom mixer is supplying a quality product to the smaller producer of molded rubber products, thus eliminating his need for expensive mixing and testing equipment.

Elastomers

The International Institute of Synthetic Rubber Producers (IISRP) indicates that total rubber consumption will increase 11% from 1988 to 1993 (10.9 to 12.1 million tons). How this increase will affect production and sales of each individual elastomer remains to be seen.

Table 2 shows the number of listings for each elastomer for these periods (Blue Book data).

There has been no change in the number of natural rubber grades over the last 10 years, however, production is estimated to increase 9.8% from 1988 to 1993. Over the last 20 year period (1968-1989), only small changes in listings occurred for the acrylics (13 to 16), chlorosulfonated polyethylene (4 to 6), polysulfides (10 to 15) and little or no change for S-B resins.

Large increases occurred for the

Table 1 - Blue Book suppliers

	1968	1980	1989
Material and ingredient suppliers	Not listed	288	344
Custom mixing	Not listed	23	57
Machinery and equipment suppliers (with products)	Not listed	275	332

ethylene-acrylics (1 to 7), EPDMs (11 to 101), fluorocarbons (10 to 75), nitriles 106 to 229), butadienes (25 to 47), chloroprenes (25 to 67), silicones (71 to 104), and especially the thermoplastic elastomers (8 to 66) and the urethanes (42 to 90).

The large growth in EPDMs is mainly due to its use in single ply roofing material. EPDM is now second in usage after the conventional roofing materials, replacing Hypalon as the most popular elastomer for this usage.

Listing decreases occurred for butyl (28 to 22), polyisoprene (13 to 8), and especially for the various types of SBR (436 to 164). This decrease for SBR shows that the number of producers is decreasing, but predicted SBR usage will increase 8.8% from 1988 to 1993, as predicted by the IISRP. It must be noted that the number of listings in many cases either indicates a reduction in the number of producers or a decrease in the grades that are available. For example, the number of black-oil masterbatches and oil masterbatches has decreased probably due to a decrease in the types of oil and blacks available.

Table 3 illustrates the rapid growth in the number of producers of thermoplastic elastomers since the production of the Solprenes in 1963 and the Kratons in 1964.

Table 2 - number of listings

Elastomer	1968	1980	1989
Natural rubber			
Standard international grades	31	35	35
TSR (SMR types)	3	9	9
Specially prepared grades	4	6	6
Modified	2	4	4
Total	40	54	54
Synthetic rubbers			
Acrylics	13	16	16
Chloronated polyethylene	0	4	14
Chorosulfonated polyethylene	4	7	6
Epichlorohydrin	2	5	8
Ethylene-acrylic	1	1	7
EPM	1	7	10
EPDM	11	50	101
Fluorocarbons	10	28	75
Butyl	28	16	22
Nitrile	106	166	229
Butadiene	25	23	47
Chloroprene	25	43	67
Polyisoprene	13	5	8
Polynorbornene	0	0	5
Polysulfides	10	8	15
Silicones	71	55	104
Synthetic rubbers			
SBRs			
Solution and block	NL	31	35
1000 (Hot)	39	25	18
1500 (Cold)	52	28	18
1600	32	17	9
1700	67	22	14
1800	74	26	29
1900	35	11	9
Cold latex	49	16	7
Hot latex	88	34	25
Styrene-isoprene	0	1	6
Thermoplastic elastomers	8	10	66
Transoctenamer	0	0	1
Urethanes	42	84	90
Vinyl acetate/ethylene	0	2	10
S-B resins	11	4	11
Reclaims and regrinds	33	33	33
Reprocessed synthetic rubber	0	7	35

Elastomer latices

Table 4 shows the listing for the various elastomeric latices over the same time period (1968-1989). For each elastomeric latex type there was a decline in the total number of listings with the disappearance of fluoro, isoprene-acrylonitrile, butadiene, butyl and isoprene latices. However, these are probably available on a special order basis. Both nitrile and SBR latices declined in their listings (45 to 16) and (25 to 13), respectively.

Elastomeric latices

In all cases there was a decline in the total listings for each latex, with the complete disappearance of fluoro, isoprene-acrylonitrile, butadiene, butyl and isoprene latices. Apparently there was insufficient demand for these products.

One of the greatest failures has been the inability of anyone to produce a synthetic polyisoprene latex with all the characteristics of natural rubber latex. The only latex listed in 1969, produced by Shell, never had all the properties desired in a latex of this type.

Although SBR listings have decreased from 25 to 13, the predicted usage of these latices will increase 8.8% from 1988 to 1993 (IISPR data).

Compounding ingredients

Table 5 shows the listings for some of the major ingredients used in elastomeric compounds for both dry rubber and latex materials. It should be noted that many of the listings for individual materials are high as there are so many forms available for the same ingredient, ie., powdered, rod-form, pastes, dispersions, elastomeric blends and micro-encapsolates, etc.

However, predicted production will increase from 382 to 400 million pounds from 1988 to 1989, according

Table 3 - thermoplastic elastomers

	Number of manufacturers		
Product type	1975	1985	1987
Polyurethane TPE	3	8	10
Styrene-diene blocks	2	3	6
Polyolefin blends	1	7	18
Styrene-EB blocks	1	1	1
Copolyester-ester	2	4	5
PVC-TPE	0	2	3
Polyamides	0	2	3
Others	1	1	4
Total	10	28	50

Table 4 - latex listings

Elastomeric latices	*1968*	*1980*	*1989*
Acrylics	19	14	22
Fluoro	0	2	0
Isoprene-acrylonitrile	0	1	0
Natural rubber	12	12	14
Nitrile	45	15	16
Chloroprene	13	14	13
Styrene-butadiene	25	50	13
Vinyl pyridine	3	7	5
Butadiene	1	0	0
Butyl	1	0	0
Isoprene	2	0	0

to a Chemical and Engineering News April 17, 1989 story. All U.S. producers (>20) are running at full or near capacity for the manufacture of these items. The C&E News article indicates that there are over 50 suppliers in the U.S. alone with some of the manufacturing in other countries. This figure does not include fillers, colorants, plasticizers and softeners. It is interesting to note that there is a trend toward supplying many of the compounding ingredients as dispersions or elastomeric blends. Some examples are shown in table 6.

Many of the dispersions are for latex use and this is especially noticeable with antidegredants and inhibitors since a large decrease has occurred since 1968. The increase in elastomeric ingredient blends reflects both the storage stability and the ease of measuring and using these materials.

The decrease in carbon black listing from 1980 to 1989 shows the effect of eliminating the manufacture of channel blacks and several grades of both thermal and furnace blacks.

In the third edition of "Rubber Technology," J.T. Byers predicts that perhaps 11 grades of carbon black have a "questionable future" and may be dropped due to decreasing use and some of the structure levels may be discontinued from manufacture.

The Blue Book in 1980 listed 40 grades as compared to 32 in the 1989 edition. Apparently the trend is continuing. The compounder must be aware of these changes and be willing to make substitutions when necessary before supplies are not available. He needs the aid of both the producer and supplier to prevent serious problems in his production of vulcanized goods. This is also important when considering all of the compounding ingredients that he uses.

Table 5 - compounding ingredients

Rubber compounding ingredients	*1968*	*1980*	*1989*
Accelerators	277	437	718
Activators	200	226	384
Retarders	25	45	47
Vulcanization agents	140	254	433
Antidegradants and inhibitors	356	341	476
Chemical and heat stabilizers	135	72	62
Homogenizers	0	4	13
Peptizers	31	14	25
Processing aids and dispersing agents	87	126	205
Tackifiers	122	166	167
Platicizers and softeners	741	570	601
Short fiber reinforcing materials	0	0	5
Carbon blacks	117	158	131
Other black materials	4	11	22
Non-blacks	362	320	423
Adhesive, bonding and sealing agents	72	147	186
Blowing agents and blow promoters	58	63	76
Dusting, dipping and washing materials	64	103	129
Finishes	0	51	62
Lubricants (molds and internal)	184	209	237
Odorants and non-staining agents	54	16	13
Latex compounding materials			
Anti-blocking agents	6	7	10
Anti-foaming agents	36	54	51
Anti-webbing agents	3	2	5
Coagulants	11	15	12
Creaming agents	1	3	1
Dispersing agents	42	39	40
Gelling agents	11	10	14
Preservatives	4	9	5
Stabilizers and emulsifiers	93	55	8
Thickening, viscosity stabilizers and reducers	19	20	26
Wetting agents	7	21	10

Summary

The usage and supply of the basic materials utilized by the compounder seem to be on an even keel since many of the items still available may function to produce a satisfactory vulcanizate, however, he has to be prepared to replace items as they are discontinued or eliminated by OSHA's requirements.

Fortunately, there are newer modifications of elastomers being developed (hydrogenated nitrile and epoxidized natural rubber are two examples) which aid the compounder in the selection of basic elastomers. In the past few decades, instrumentation has been computerized to the point where mixing, processing, vulcanization and testing data is stored and can be recalled when needed.

This type of instrumentation, curemeters for example, has greatly aided the compounder in developing compounds and aids in maintaining quality control of production items, as the search for uniformity will continue.

Table 6 - blends and dispersions

		1968	*1980*	*1989*
		Listings available		
Accelerators	Dispersions	35	56	67
	Elastomer blends	39	134	183
Activators	Dispersions	8	42	38
	Elastomer blends	11	57	69
Vulcanization agents	Dispersions	16	40	39
	Elastomer blends	13	79	89
Antidegradants and inhibitors	Dispersions	50	15	13
	Elastomer blends	0	4	12